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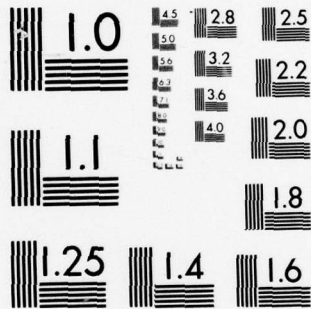
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RADIATION EFFECTS ON MOS/SOS SEMICONDUCTOR DEVICES

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ABSTRACT

Measurements have been made on radiation induced leakage
currents in MOS/SOS structures and the effects of optical bleaching
and further irradiation under zero bias conditions have been studied.
In order to understand the role played by bulk traps in Al_2O_3 in the
radiation induced leakage currents and to identify the possible lattice
defects associated with these traps, Thermally Stimulated Current Tech-
niques have been employed. Optical bleaching and trap repopulation
studies have been made in conjunction with the thermally stimulated
current measurements.

A review of data on trapping states in Al_2O_3 is presented and
models for the trapping and charge compensation processes involved in
the back channel leakage are discussed.

Introduction

The fabrication of CMOS circuits using SOS technology has a number of advantages from the point of view of their response to an ionizing radiation environment. The presence of an "inert" substrate, such as the Al_2O_3, reduces unwanted circuit capacitance and consequently reduces the dynamic power requirements of the circuits and increases device speed. The inherent dielectric isolation provided by the substrate obviates the need for the device isolation zones necessary in bulk silicon structures and therefore permits higher packing densities with potentially lower device costs. In the presence of a radiation flux, transient photocurrents are reduced and the isolation of the individual devices by an insulating substrate reduces "latch up" problems due to parasitic bipolar transistors. The above considerations suggest that CMOS/SOS devices might be well suited to applications where radiation fluxes could be encountered. However, one problem associated with this device configuration tends to negate the advantages outlined above.

In CMOS/SOS structures the active volumes of the silicon extend to the heterojunction with the Al_2O_3. Sapphire is a wide band gap insulator and when exposed to ionizing radiation(photons of 10 eV or greater energy) electron/ hole pairs are generated and trapping of these carriers may occur in the region of the heterojunction. Under the influence of the fringing fields from the CMOS device an imbalance between the trapped positive and negative charge is created and a net positive charge accumulates in the region of the heterojunction. This charge has the effect of creating an n-channel in the Silicon at the silicon-sapphire interface and consequently the leakage current associated with n-channel transistors may be increased by several orders of magnitude due to this "back channel" leakage. In addition, charge stored in the gate oxide of the device may cause a change in the threshold and so at zero gate voltage the front channel

of the transistor may also contribute to the leakage current. As has been pointed out by Berkan[1] these combined currents may increase the source to drain leakage in the "off" condition by as much as four orders of magnitude.

The radiation sensitivity of CMOS/SOS structures appears to be dependent upon the conditions under which they are fabricated with both the silicon deposition step and subsequent processing stages such as gate oxide growth being important. In general, lower temperature processing conditions and shorter exposures to elevated temperatures seems to improve device radiation resistance provided the quality of the structure can be maintained[2].

The research, summarized below has been directed at obtaining an understanding of the nature and stability of electronically active traps in Al_2O_3, their relationship to the back channel leakage currents following irradiation and the possible effects of device processing parameters on the trap densities. In the first section the nature of trapping centers in Al_2O_3 is discussed. In Section II the effect of possible interactions at the Si/Al_2O_3 interface on the Al_2O_3 structure and on local trapping states is reviewed. Section III contains an account of experimental measurements made on both MOS/SOS structures and bulk Al_2O_3 in an attempt to understand which defect centers may play a role in the back channel leakage process. The last section contains a discussion of these measurements and comments on the expected effects of processing parameters on the back channel leakage.

I. Hole and Electron Traps in Al_2O_3

Hole traps in Al_2O_3 have received extensive experimental attention using ESR[3,4,5], optical[5,6,7,8], Thermoluminescence[6,7,9] and Thermally Stimulated[10,11] current techniques. The nature of the physical defects in the Al_2O_3 lattice acting as the trapping sites have largely been postulated on the

basis of the ESR measurements. In general, these defects contain an aluminum vacancy and the trapped holes are associated with changes in the charge state of oxygen ions adjacent to the aluminum vacancy site. Despite the largely ionic nature of the bonding in Al_2O_3 it is convenient to visualize the lattice as being constructed from "molecules" of Al_2O_3 as indicated in Fig. 1. The two Al^{3+} ions lie along the c-axis of the crystal and the triangle of oxygen (2-) ions is at their midpoint. Along the c-axis "molecules" of this type are separated by a void site and as a result of the pseudo-hexagonal structure of Al_2O_3 each molecule along the axis is rotated by 60° with respect to its neighbors. When one of the Al^{3+} ions of this "molecule" is missing, the molecule may trap holes on the oxygen ion sites (Fig. 1b). The V^{2-}-center involves a single hole at such a location and the V^--center is the same defect that has trapped two holes. Prior to trapping holes this defect has a negative effective charge in the lattice and even when occupied by two holes would still be expected to be a negatively charged center or perhaps neutral.

Hydroxyl impurities can be incorporated into the Al_2O_3 lattice substitutionally on oxygen ion sites (Fig. 1b). When such an OH^- ion is adjacent to an aluminum vacancy this pair of point defects is still able to capture holes and the corresponding defect is known as the V_{OH}^--center. Once again this defect array in the lattice has an effective negative charge even when occupied by a hole.

The optical properties and thermal stability of hole defects of this type have been extensively studied. All of these hole centers are associated with optical absorption in the spectral region between 2.5 and 3.0 eV. From optical absorption and thermal bleaching experiments Turner and Crawford[6,7] concluded that the V_{OH}^-- center can be thermally bleached at circa 400K and that

the thermoluminescence that accompanies this process is due to the hole being captured by a chromium impurity in the crystal with a corresponding change in valence state; $(Cr^{2+} + h \rightarrow Cr^{3+} + h\nu)$.

The two hole V^--center may also be thermally bleached and Lee and Crawford[12] indicate that such bleaching occurs at <u>circa</u> 370K with a V^{2-} defect being left at the same location. This V^{2-}-center is stable thermally until about 500K at which temperature the second hole is released from the trap. These temperatures are too low to modify the defect structure and these defects can therefore be repopulated by subsequent exposure to ionizing radiation.

The hole centers discussed above are similar to those that exist in MgO[13]. In this lattice the cation vacancies associated with the hole traps are introduced into the lattice as charge compensators for ionic impurities such as Al^{3+}, Si^{4+} etc., and it is to be expected that a similar process would occur in Al_2O_3 to compensate aliovalent cation impurities. The calculations of defect formation energies in Al_2O_3 by Dienes et al.[14] would indicate that compensation of excess positive charge by Al^{3+} vacancy formation would be favored over charge compensation by oxygen interstitials with their respective creation energies, calculated on a polarizable point-ion shell model, being 8.0 and 10.2 eV. It has been found in MgO that as the concentration of aliovalent cations increases the number of holes trapped at V-type defects in the lattice saturates since the ionic impurities can change their valence state and therefore compete with the cation vacancy defects as hole traps. Similar behavior seems to occur in Al_2O_3 and on the basis of EPR and thermal conductivity data Brown[15] and Abou-Ghantous, et al.[16] report chromium impurity ions in Al_2O_3 with both a 4+ and 5+ charge. Neutron activation analysis measurements[17] on Linde Al_2O_3 indicate that Cr, Fe, Na and Zn are all present in concentrations greater than 1μg/gm.

Lee et al.[5] have studied the sensitivity of substitutional Cr^{3+} and Fe^{3+} to γ irradiation. After an exposure to about 2×10^5 R of Cs^{137} γ rays about 25% of the Cr^{3+} ions have been converted to either the 2+ or 4+ state through electron or hole capture, however, the Fe^{3+} defects exhibited no change in valence state. Thermal bleaching studies showed that the changed valence state of the Cr ions was stable until about 550K at which temperature the Cr^{3+} signal increased and a thermoluminescence peak was observed.

In Al_2O_3 that has been exposed to particle bombardment (which can create oxygen vacancies) the oxygen vacancy sites can also act as electron traps. A vacancy occupied by two electrons is the F-center and has an optical absorption band at 6.1 eV. The singly occupied vacancy is the F^+-center and its associated optical absorption occurs at 4.8 eV. Lee and Crawford[12] and Turner and Crawford[7] have studied the radiation filling and the optical and thermal bleaching of these defect centers. The optical bleaching studies indicate that the F-centers may capture free holes to become F^+-centers. During γ irradiation the 6.1 eV band and the V-centers increase in parallel and the saturation behavior of these two bands indicates that the presence of the hole traps restricts electron-hole pair recombination processes and makes electrons available for the oxygen vacancy centers.

Measurements on the threshold energy for oxygen vacancy creation were made by Arnold and Compton[18] who studied the growth of the 6.1 eV optical absorption band in crystals subjected to bombardment by energetic electrons. The displacement threshold for oxygen ions was found to be 90 ± 5 eV, the corresponding electron energy being 430 KeV. Arnold et al.[19] have studied ion implantation induced lattice displacements in Al_2O_3 and have shown that F-center defects are produced upon bombardment with light ions in the 50 → 100 KeV range. The ionization intensity associated with the ion bombardment was also

found to be important with the defect yield being greatest for light ions such as H^+ and D^+. As expected a volume expansion was produced by the creation of oxygen Frenkel pairs in the lattice and this volume expansion was found to be sensitive to the charge state of the defects. When the oxygen vacancies are occupied by electrons their associated lattice distortion is reduced.

From the point of view of SOS technology the papers discussed above indicate that both hole and electron traps associated with point defects in the sapphire matrix are to be expected. Typical point defect densities in nominally pure bulk sapphire are on the order of $10^{15} cm^{-3}$ for V_{OH}^- type defects and $10^{16} \rightarrow 10^{17} cm^{-3}$ for ions capable of changing their valence state. This number may be modified at the silicon Al_2O_3 heterojunction by interactions between the epitaxial silicon and the aluminum oxide substrate that occur during the epitaxial deposition of the silicon and also during subsequent device processing stages.

II. The Interfacial Region at the Si/Al$_2$O$_3$ Hetrojunction

In terms of the leakage current it produces, charge trapping in the proximity of the heterojunction between Al_2O_3 and Si is more important than a similar density of trapped charge in the bulk of the Al_2O_3. Srour, et al.[20] have made measurements on electron beam induced back channel leakage currents in SOS structures and have determined that energy must be deposited in the Al_2O_3 by the electron beam in order to increase the leakage current. They conclude that the most important region of the sapphire substrate lies within 2μ of the Si/Al_2O_3 surface. Excess holes are trapped in this region either because the fringing fields due to the MOS device remove electrons from the region or because the density of hole traps is largest near the interface.

The interface between silicon and sapphire has received considerable experimental attention, however, there still seems to be uncertainty concerning the existance of an intermediate insulating zone between the silicon and the Al_2O_3. Cullen and coworkers[21] conclude that there is no intermediate zone at the heterojunction although the first 500 Å of the epitaxial silicon does not have bulk structure. During chemical vapor deposition of silicon at substrate temperatures on the order of 980°C, silicon reacts with the Al_2O_3 and may create volatile oxides such as SiO or Al_2O together with metallic aluminum. Cullis and Booker[22] suggest that this may give rise to an interfacial alumino-silicate through a reaction of the type:

$$Si + Al_2O_3 \rightarrow Al_2SiO_5 + Al_2O(g).$$
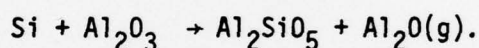
Presumably this type of reaction can continue until the silicon islands nucleated on the sapphire grow together and prevent the further escape of the volatile products. Typically, this corresponds to a silicon overlayer on the order of 500 Å in thickness. Film growth rates of 3μ of silicon per minute are commonly used and silicon layers of $0.6 \rightarrow 1.0\mu$ are employed for device fabrication. On the basis of the growth time and temperature it is therefore to be expected that little solid state transport from this reaction zone into the Al_2O_3 is likely to occur during the deposition process. The modified surface layer produced by the deposition process is, however, closest to the back channel region and may therefore be important in the radiation response of devices.

Harari and McGreivy[23] have considered the effect of an interfacial region on the Silicon side of the Al_2O_3/Si heterojunction on the back channel leakage current. Using channels of different length and employing ionizing radiation and optical bleaching techniques to alter the back channel leakage

behavior, they conclude that the higher leakage currents in devices with dry oxide do not result from the same source as the radiation induced leakage currents and are probably due to an n-type conducting layer at the Si/Al_2O_3 interface. The radiation induced component of the leakage current is associated with positive charges trapped in the Al_2O_3. These charges will tend to invert the silicon layer at the interface and since the "dry oxide" devices already have a slightly n-type character, these will be more strongly turned on by a given sapphire charge storage. Deliberate doping of the back channel region with boron reduces the leakage currents and if the traps in the Al_2O_3 are limited in number it could be possible for trap saturation to occur before the threshold voltage of the back channel transistor is reached.

After the thermal deposition of Si on Al_2O_3 the device processing steps involve exposure to high temperatures for various time periods. Maldonado et al.[24] have considered the redistribution of impurities in the Silicon that may result from such high temperature processing but have treated the Silicon-Sapphire interface as "reflecting" for the impurity species, the sapphire remaining unchanged on this model.

Little data is available on the diffusion of ions in single crystal sapphire. Oishi and Kingery[25] have measured the diffusion of Oxygen in sapphire and find a diffusion coefficient on the order of $10^{-15} cm^2 sec^{-1}$ at temperatures of circa $1000°C$. On the basis of measurements on polycrystalline Al_2O_3 by Paladino and Kingery[26] a similar value for the self diffusion coefficient of Aluminum in single crystal Al_2O_3 might be expected. While these values of the diffusion coefficient are low they do indicate that diffusion into the Al_2O_3 can take place at the temperatures associated with oxidation steps in device processing. If it is assumed that an impurity (such as silicon or boron) has a diffusion coefficient equal to that measured for oxygen and that

the surface concentration of this impurity is constant during the diffusion process, then, under the conditions of dry oxidation (150 mins at 1273K) a penetration depth of 100 Å is to be expected. For wet oxidation conditions (60 mins at 1190K) the impurity would only penetrate 30 Å into the Al_2O_3.

This transport of material from the Silicon overlayer into the Al_2O_3 may also alter the local crystal structure of the heterojunction. Amaraki and Roy[27] determined the Al_2O_3 - SiO_2 binary phase diagram for temperatures above 1400°C. At the Al_2O_3 rich end of this diagram Mullite (3 Al_2O_3:2 SiO_2) and Al_2O_3 coexist as a two phase solid solution. MacDowell and Beal[28] have extrapolated this diagram to lower temperatures and in the Al_2O_3-rich end of the diagram no additional phase separation is expected to occur. It therefore seems probable that in the region of the Si/Al_2O_3 heterojunction regions of different chemical composition such as Mullite or an alumino-silicate such as Al_2SiO_5 may occur. Such regions may alter the local hole trapping density in the oxide at the interface. A comparison between traps in Al_2O_3 and in Spinel ($MgAl_2O_4$) by White et al.[29] suggests that they may be of a similar structure. It is also to be expected that mullite and Al_2SiO_5 will provide defect sites capable of trapping electrons and holes that are similar to those of Al_2O_3.

III. Experimental Results

Experimental measurements have been made on MOS/SOS samples of two types and also on bulk Al_2O_3 from a number of different sources. The MOS measurements were directed at understanding the back channel leakage currents, their dependence upon X-irradiation conditions and the thermal and optical stability of the associated trapping levels. The measurements on bulk Al_2O_3 were made in order to understand electron and hole trapping in this material and to

evaluate the importance of the various traps for the back channel leakage
behavior.

   a) MOS/SOS measurements

   Back channel leakage current measurements have been made on two types
of MOS/SOS structures. One set of measurements was made on n-channel 4007
type test structures fabricated at Hughes Aircraft. These had a wet gate oxide
approximately 950 $\overset{o}{A}$ thick, a channel width of 40 mils and a channel length of
0.3 mils. The starting material for these devices was fabricated by Union
Carbide with {100} silicon grown epitaxially on {1$\bar{1}$02} sapphire. The indi-
vidual 4007 chips were mounted in ceramic packages with a hole drilled in the
base so that light could illuminate the heterojunction from the sapphire side.

   Another set of n-channel test structures was also fabricated at Hughes
Aircraft and designated NORT 21. Samples from this same batch have been
studied by Srour et al.[20]. Again the source of the starting material was
Union Carbide. Test transistors were fabricated with the channels making
different directions with respect to the sapphire substrate. Processing was
identical for two groups of these structures with the exception of the oxida-
tion step. One group had a pyrogenic (wet) oxide about 980 $\overset{o}{A}$ in thickness
grown at 925°C while another group had a dry oxide about 930 $\overset{o}{A}$ thick produced
at a temperature of 1000°C. Aluminum gate metallization was used on both sets
of structures and so as to be suitable for the electron beam studies of Srour
et al. this metallization was only 750 ± 100 $\overset{o}{A}$ in thickness. All the devices
had a channel length of 0.2 mils and a channel width of 8.0 mils. These devices
were also mounted on DIP packs which had had a hole drilled in the substrate so
that the device could be illuminated through the sapphire.

   Back channel leakage currents were induced in these devices by
exposing them to 90 KeV X-rays from a tungsten target tube. Total doses

between 10^5 and 10^6 rads (Si) were employed, the devices being exposed through the silicon over-layer. X-rays of this energy have insufficient energy to create new traps in crystalline Al_2O_3 and so the back channel leakage currents result from charges trapped at pre-existing defects. During X-irradiation the source was held at ground potential. Typically, for the 4007 structures $V_{DS} = V_{GS} = 10$ volts during the irradiation and for the NORT 21 samples $V_{GS} = 0$ and $V_{DS} = 4$ volts.

Leakage currents both before and after X-irradiation were measured with a Keithly 616 digital electrometer with a current sensitivity of 10^{-15} amps. Steady bias voltages to the structures were provided by an HP 6299A regulated power supply and a home made voltage ramp was used to sweep either V_{DS} or V_{GS} depending on the measurement being made.

Typical data for the leakage current induced by X-irradiation in a 4007 type structure is shown in Fig. 2. Prior to any X-irradiation the source to drain leakage currents with $V_{DS} = 3$ volts and $V_{GS} = -5$ volts were on the order of 4×10^{-10} amps. For this value of V_{GS} the front channel transistor is in the "off" condition and the source to drain leakage current is all associated with the back channel. After 10^5 rads Si the leakage current under the same bias condition had increased to about 8×10^{-6} amps. The threshold shift of the front transistor was small enough that it was still in the "off" state under the conditions of measurement. By exposing such a sample to the full radiation from a Xenon light source for circa 10 mins. with $V_{GS} = V_{DS} = 0$ it was found that the leakage current could be reduced to its preirradiation value. It was also found that a further exposure of the sample to X-rays but with all electrodes at ground potential would reduce the back channel leakage currents to approximately that of an unirradiated sample Similar data was obtained for both the Wet and Dry Oxide NORT 21 samples. Exposure to circa 10^5

rads (Si) increased the back channel leakage currents by about two orders of magnitude. Reirradiation with all electrodes at ground potential reduced these currents to essentially their pre-irradiation values. Illumination of these devices with Xenon light could also be used to remove the radiation induced leakage currents.

Both the Xenon light and the X-rays are capable of injecting electrons into the Al_2O_3 from the Si and these may neutralize the trapped holes at the heterojunction and produce the observed reduction in leakage current. The U-V photons may also release holes from their traps in the Al_2O_3 and these may move under the influence of their mutual interaction either into the bulk of the Al_2O_3 or to the Silicon. In either case the back channel leakage current should be reduced. In order to determine if this photodepopulation process was occurring and to obtain a measure of the optical depth of the associated hole traps, measurements were made in which a monochromator was used to provide photons of a given energy and the effect of these photons on the X-ray induced leakage currents was studied. Fig. 3 shows the results of such optical bleach- ing studies made on 4007 structures. After X-irradiation the back channel leakage current was circa 20μA with V_{DS} = 3 volts and V_{GS} = -5 volts. Each data point presented corresponds to the leakage current measured under these same conditions after the specimen had been illuminated with photons of the indicated energy for two mins. with all electrodes connected to ground. The data points therefore represent the cummulative effect of all exposures at that photon energy and lower energies. It is seen from the diagram that the leakage current starts to decrease for photons having energies greater than 2.1 eV and that the maximum bleaching rate occurs for photons of about 2.5 eV. If photons of 2.5 eV are employed following a room temperature X-irradiation,

the time dependence of the decay of the radiation induced leakage currents has the form shown in Fig. 4. Photons of this energy are not capable of injecting electrons into the Al_2O_3 from the silicon and these measurements therefore suggest that the trapped charges responsible for inducing the leakage currents are either directly bleached by the photons or removed from the interface zone by recombination with electrons released from other trap levels in the Al_2O_3. The measurements reported below on bulk Al_2O_3 were designed to clarify this point.

It was also found that the radiation induced leakage currents could be reduced if the samples were thermally annealed. Fig. 5 shows some thermal annealing data for the 4007 structures. The structures were maintained at the temperatures indicated on the curves for the times corresponding to each data point, however, the actual leakage current measurements were made at room temperature to avoid effects due to the temperature dependence of the channel mobility and the Fermi level in the semiconductor. On the basis of these curves an estimate of the thermal depth of the hole traps (or corresponding complementary electron trap) can be made using the method of cross cuts[30] and was found to be circa 0.8 eV.

Measurements made on the NORT 21 samples were less complete than those on the 4007 structures since only a limited number of devices was available and the yield of good transistors on a chip was low. The spectral dependence of the leakage current bleaching behavior for the wet and dry oxides was essentially the same and again indicated that photons of between 2.0 and 2.5 eV were capable of removing charge stored in the Al_2O_3 substrates. No thermal bleaching measurements were made on these samples although a time dependence of the leakage currents immediately following X-irradiation suggested the presence of some shallow hole traps in these samples.

b) <u>Bulk Al_2O_3 measurements</u>

The measurements reported above indicate that a knowledge of the trap structure of Al_2O_3 is desirable if the effects of X-irradiation and optical bleaching on the charge storage that affects the back channel leakage currents is to be understood. To this end thermally stimulated current measurements[31] were used to characterize traps in Al_2O_3 that could be populated by X-irradiation. Optical bleaching and trap refilling measurements were also combined with the TSC technique to provide information about the charge redistribution in the material produced by the photons.

Samples of Al_2O_3 single crystals were obtained from three sources since it is to be expected that both the impurities present in the lattice and the lattice stoichiometry will be affected by the purity of the starting materials and the details of the growth processes.

Single crystal discs 1 mm thick x 160 mm dia. were obtained from R. W. Klaffky of Brookhaven National Laboratories. Both of these were nominally pure samples, one being cut from starting material produced by the Linde Company, the other from the A. Meller Company. Samples in the form of rectangular plates 0.3 mm x 9 mm x 19 mm were purchased from the Insaco Corporation. The starting material for these samples was also grown by Linde.

Electrodes in the form of circular guarded parallel plates were put onto these samples either by sputtering (Pt or Pd) or by vacuum evaporation (Al). Current measurements were made using a Cary 401 vibrating reed electrometer. The heating rate following an X-irradiation was typically 12 K min^{-1} and it is estimated that a temperature gradient of no more than 5 K exists in the sample at this heating rate.

In order to populate the hole and electron traps in the Al_2O_3, samples were exposed to 100 KeV X-rays from a tungsten target tube. Exploratory

measurements indicated that an exposure of about 10^5 rads (Si) was adequate to saturate the traps in the material at either room temperature of liquid nitrogen temperature. The TSC measurements were made with a bias of 5 volts applied to the MIM structure. Again exploratory measurements indicated that the magnitude of the current peaks increased linearly with the applied bias but no additional peaks were observed up to the maximum bias of 80 volts that was employed. The 5 volt bias level was therfore chosen as a suitable compromise between signal current and noise.

As indicated in Fig. 6 following irradiation at 78K samples from all three sources show a series of TSC peaks with maxima between 200 and 700K. If a sample was cooled to liquid nitrogen temperature immediately after such a TSC run and then taken through the same warmup cycle under bias no TSC peaks were observable. All of the spectra show a large peak at 273K. The Linde and Insaco samples show rather similar peak structures and these differ considerably from that of the Meller sample. The peak spectrum of the Meller sample is, however, the same as that reported by Fullerton and Moran[32] for samples from the same source in the region above room temperature where the two sets of data can be compared.

Within the set of Insaco samples examined there is some variability in the TSC peaks that are obtained. Only the 273K peak is present in all samples, however, TSC peaks at 210, 368, 407, 506, and 562K also occur in two or more samples. These peaks are not dependent upon the electrode material employed and are reproducible for a given sample following electrode removal and redeposition.

In order to determine the activation energies and frequency factors associated with the traps responsible for the main TSC peaks, a peak cleaning technique was used to remove the influence of low temperature peaks from those

at a higher temperature. The heating rate, the temperature of the current maximum and the low temperature half width of each of the peaks were determined and this data used in conjunction with the analytical method of Chen[31] to compute the trap parameters. These are summarized in Table 1. Assuming first order kinetics and a constant pre-exponential factor, the trap depth is given by:

$$E = \frac{1.52 \ k \ T_{max}^2}{T_{max} - T_{\frac{1}{2}}} - 1.58(2 \ kT_{max}).eV$$

and the frequency factor by:

$$S = (\beta E/kT_{max}^2) \ exp(E/kT_{max}).sec^{-1}$$

where β is the heating rate in K/sec.

The error estimates associated with the activation energies arise from uncertainties in the peak temperature and that of the low temperature half width. The frequency factors given are only reproducible for a given sample to an order of magnitude.

From the point of view of the back channel leakage currents it is mainly the TSC peaks that appear near room temperature that are of interest since the thermal annealing studies on the 4007 structures indicated that heating to 90°C reduced these leakage currents, presumably due to thermal emptying of the trap levels.

In order to obtain a better understanding of the traps and carrier types associated with the Thermally Stimulated Current peaks optical bleach-ing methods were used. The traps in a sample were populated with carriers by X-irradiating at either liquid nitrogen or room temperature. The sample was then exposed to photons from a 150 W Xenon light source, the energy of which

was selected either by the use of filters or a Bausch and Lomb high intensity monochromator operated with a 12 nm pass band. The unfiltered Xenon light source had an intensity of circa 300 mw/cm^2 at the sample surface. The filters were of Corning glass and had a transmission of 85 to 90%. At 3.0 eV the output of the monochromator was circa 9 mw.

Because of the metal electrodes for the current measurements it was necessary to illuminate the samples through their edges. The optical density of the samples was low over the entire spectral range examined and so the active volume between the electrodes was uniformly illuminated. After a chosen period of illumination at a given wavelength the TSC spectrum was taken and the peak heights compared to those for the same sample that had received no exposure to light. This procedure was repeated at a series of wavelengths in order to determine the threshold energy for bleaching of the individual peaks.

Figure 7 shows data obtained for the Meller sample using filters in conjunction with the Xenon light source. The data points are plotted at that energy corresponding to the maximum photon energy transmitted by the filter. The sample was X-irradiated at room temperature for 5 min. at 100 KeV and 20 mA prior to each TSC measurement. The bleaching time at each energy was 5 mins. It is seen that the 372K peak is bleached for all wavelengths used; that the 437K peak remains essentially unchanged until a photon energy greater than 3.2 eV after which it <u>increases</u> in magnitude; the 495K peak remains unchanged for all the photon energies used and the 560K peak shows a decrease for all wavelengths used. It is interesting to note, however, that the 560K peak shows a <u>smaller</u> decrease when exposed to the full radiation from the Xenon source than when exposed to photons having a maximum energy of 4.1 eV. Similar measurements made after a liquid nitrogen temperature X-irradiation and optical

bleaching exposure indicated that the peak at 273K was not bleached with full light from the Xenon source. This behavior was verified using the high intensity monochromator and the threshold wavelengths for trap modification determined. This data is presented in Table 2.

Similar measurements were made on the Linde sample following both liquid nitrogen and room temperature X-irradiation. For this sample also the 273K peak was unbleached by full Xenon light, the 365 peak bleached with 1.5 eV light, the 405K peak with 2.5 eV light, the 504 peak with 2.1 eV light and the 576K peak showed no bleaching even with the full Xenon light.

It seems clear that in both samples charge redistribution among trapping levels is taking place. A comparison between the thermal activation energies of the traps and the optical threshold for their bleaching suggests that the photons may not be interacting directly with the trapping levels responsible for the TSC peaks but with other levels in the Al_2O_3. In order to investigate this charge redistribution further, samples that had been X-irradiated and then had their TSC traps emptied by heating to 650K were cooled to low temperatures, exposed to photons of various energies and their TSC spectra retaken. By using the monochromator in conjunction with the Xenon light source it was possible to detect the threshold photon energy that caused refilling of a given TSC level.

For the Meller sample only three of the TSC peaks could be regenerated in this way. The peak at 437K had been found by Fullerton and Moran to be extremely sensitive to X-ray dose. This peak reappeared in the TSC spectrum at the lowest photon energy (2.3 ± 0.1 eV) and grew to its saturated value very rapidly. After only 10 secs of exposure to light from the Xenon source the peak had reached approximately 30% of its saturation size. The peaks at 273K

could be restored with photons having energies of 2.7 ± 0.1 eV. No other TSC peaks could be restored even after exposure of the sample to the full radiation from the Xenon source. This redistribution of charges among trap levels in the Al_2O_3 could be performed many times. Once the material had been exposed to X-irradiation the TSC traps indicated above could be repeatedly filled by exposure of the sample to light and then emptied thermally. This cycling has been continued for several days with no apparent changes in the magnitudes of the TSC peaks following a given exposure to light.

The behavior of the Linde sample under the same trap repopulation conditions was somewhat different. The 273K peak could not be regenerated, even with the full light from the Xenon source. A peak at 437K that was not apparent in the TSC spectrum after X-irradiation alone was obtained after exposure to photons having energies greater than 2.7 eV and the peak at 576K was regenerated with these same photon energies. For this case also thermal depopulation and optical refilling of these traps could be taken through many cycles over an extended time period.

IV. Discussion

The measurements on MOS/SOS structures reported above indicate that the back channel leakage currents produced by exposure of the devices to ionizing radiation result from charge storage in the Al_2O_3. This excess positive charge situated near the Al_2O_3-Si heterojunction can be neutralized by the injection of electrons into the sapphire, as suggested by the reduction of the leakage currents following further exposure to X-irradiation with all electrodes grounded. The experiments with low energy photons (~2.5 eV) indicate that the excess positive charge at the heterojunction can also be reduced either through

the photodepopulation of traps at the interface to alter their charge state or by the production of free carriers from other traps in the Al_2O_3 that can then change the charge state of those traps responsible for the leakage currents. The thermally stimulated current measurements made on bulk Al_2O_3 specimens indicate that the trap structure of this material is complex and that low energy photons do, in fact, produce charge redistribution among the various trapping levels. It is also apparent from these measurements that Al_2O_3 produced by different vendors has a different trap structure. If the traps near the heterojunction are the same as bulk traps but are differently populated due to the fringing fields from the MOS structure, then the source of Al_2O_3 used for device fabrication might significantly change their radiation hardness. Measurements on bulk Al_2O_3 may not properly characterize the traps at the heterojunction since it is to be expected that the sapphire as well as the silicon will be modified during silicon deposition and device processing. Estimates of the diffusion depth of impurities into the Al_2O_3 that could occur during the oxidation steps of device fabrication show that for dry oxidation conditions penetrations on the order of $100 \overset{o}{A}$ are possible. Since this modified region is closest to the heterojunction charge trapping in it will have the maximum effect on the leakage behavior. For a wet oxide the penetration depth of impurities is only about $30 \overset{o}{A}$ and consequently the number of diffusion associated traps at the heterojunction that are "seen" by the silicon may be reduced by about a factor of three. This may be partly responsible for the lower leakage currents observed in devices that have had low temperature processing.

That the major trap level in Al_2O_3 associated with the back channel leakage currents can have its charge state altered when the material is

illuminated with 2.5 eV photons now seems to be well established, at least
for devices based on Union Carbide SOS starting material. Williams et al.[33]
have reported the optical bleaching of traps with photons of this energy.
Prior measurements by Harari[34] had suggested that electron injection from
the Silicon was required to neutralize the charges in the sapphire, however
subsequent discussions suggest that the low intensity of the monochromatic
light used in these measurements was responsible for this observation[23].
It is well known that hole centers in Al_2O_3 such as V^{2-}, V^- and V_{OH}^- have an
associated optical absorption in the 2.5 → 3.0 eV region and it therefore
seems probable that the photons are in fact bleaching hole traps in the Al_2O_3.
On the basis of the thermal stability of the traps associated with the back
channel leakage currents it would be expected that they should give rise to
thermally stimulated current peaks at temperatures close to 100°C. The Linde
derived samples used in these measurements exhibit two TSC peaks in this
temperature range one at circa 365K and the other at 405K. The activation
energies determined for these trapping levels from an analysis of the TSC peaks
are 0.8 ± 0.1 eV and 0.85 ± 0.1 eV respectively. These are both close to the
value of 0.8 ± 0.1 eV determined from the isothermal annealing data on irradiated
MOS/SOS structures. Optical bleaching measurements on the bulk Al_2O_3 indicate
that the 365K peak in the TSC spectrum has a bleaching threshold of 1.5 eV while
for the 405K peak the bleaching threshold is at 2.5 eV. Both of these trap
levels could therefore be optically bleached by photons of the energy that was
found to reduce the back channel leakage in irradiated MOS/SOS devices.

The nature of the lattice defects associated with the TSC measurements
can be inferred by a comparison of the present data with previous esr, thermo-
luminescence and optical studies. The TSC spectra of the Meller sample have

the simplest form and seem to be most directly related to prior data of this type. The V⁻center in Al_2O_3 is known to anneal thermally at about 370K and to have an associated optical absorption in the spectral region between 2.2 and 3.5 eV. This suggests that the 372K peak observed in the TSC spectrum of the Meller sample is associated with the V⁻defect, this trap having a thermal depth of 1.1 ± 0.1 eV. When this trap is populated by X-irradiation, bleaching with 2.4 eV light is found to reduce the magnitude of the 372K peak but to leave the height of the 495K peak unchanged. If the 495K peak in the TSC spectrum is associated with the V^{2-}center, which is known to thermally anneal near 500K, this behavior is to be expected. The 2.4 eV light removes one hole from the V⁻defect converting it to the V^{2-}defect. The size of the TSC peak associated with the V⁻defect should therefore decrease but the size of the V^{2-}peak should remain the same since it is not important whether the first hole is removed from this site thermally or optically.

The optical trap repopulation experiments following a thermal emptying of the TSC peaks did not result in the repopulation of the two levels discussed above. Those peaks which occurred at 273, 437 and 560K were regenerated, suggesting that they may be associated with electrons rather than holes. The peak at 437K was found to be extremely sensitive to X-ray or photon repopulation in the present measurements. Fullerton and Moran[32] also found this to be the case which suggests that the associated defect center has a large capture cross-section for electrons. It is interesting to note that the threshold energy for photo-repopulation of this level is circa 2.4 eV suggesting the presence of an electron trap at this level that is not thermally depopulated. This corresponds to the photon energy at which the 372K peak may be optically bleached and may indicate that this center is capturing an electron and being converted to the

one hole V^{2-} center. Presumably further electron capture by the defect is prevented by the large effective negative charge of the V^{2-} site.

The 273 and 560K peaks are repopulated by photons of 2.7 and 2.9 eV respectively, presumably from deep electron traps since the photoinjection threshold from the metal electrodes should be on the order of 4 to 5 eV.

In a sample that has not been thermally bleached following X-irradiation the 273K peak cannot be optically bleached, the band at 560K starts to bleach at photon energies greater than 2.6 eV and the 437K peak increases in size when the sample is exposed to photons of energy greater than 3.5 eV. As shown in Fig. 7 the bleaching of the 560K peak produced by equal exposures to photons of increasing energy increases as the photon energy increases up to 4.1 eV. However, when the sample is exposed to the full radiation from a Xenon source, which photocurrent measurements suggest is causing photoinjection from the electrodes, this peak is bleached less than by the 4.1 eV photons. This would indicate that the observed bleaching involves a balance between hole and electron capture at this defect with the high electron density produced by photoinjection dominating the behavior at high photon energies. The 437K peak, which has been postulated to have a large cross-section for electron capture, starts to increase in magnitude for photon energies larger than 3.5 eV. Lee and Crawford[12] have associated an absorption band at this energy with a trapped electron center, and electrons liberated from this level may be repopulating the 437K trap. The 437K peak has its largest magnitude when the threshold energy for electron internal photoemission from the electrodes is passed.

The TSC spectra for the Linde samples are more complex and the effects of the optical bleaching of the associated traps are also harder to interpret.

A comparison between the TSC spectra for the Linde and Meller samples would suggest that the peak at 273K is due to the same defect in each case. Following X-irradiation, optical bleaching (even with the full Xenon light) produced no change in the magnitude of this peak in samples from either source. However, whereas this defect level may be repopulated with 2.7 eV photons following thermal bleaching in the Meller sample, no repopulation occurs in the Linde samples even with photons capable of causing internal photoemission of electrons from the electrodes. Photons with energies greater than 2.7 eV do, however, produce two peaks in the Linde samples, one at 437K, which corresponds to a peak in the TSC spectrum of the Meller sample that was not found in the Linde TSC spectrum following just X-irradiation, and one at 576K. This last peak was one that could not be optically bleached following X-irradiation even with the full Xenon light. On the basis of the discussion above it would seem that these two peaks are associated with trapped electrons.

The reason for the nonappearance of the 270K peak is not clear. Kristianpoller and Rehavi[9] in thermo-luminescence studies of Insaco sapphire have reported major thermoluminescence peaks at 250, 310 and 450K. They assign the 250 and 450K peaks to hole traps and the 310K peak to an electron trap. If their 250K peak corresponds to the 273K TSC peak obtained in the present measurements this would imply that the latter is due to a hole center and its nonappearance in the optical repopulation experiments might therefore be expected. However, it is then hard to understand the stability of this center to optical bleaching in an X-irradiated sample and its optical regeneration in the Meller samples together with apparent electron centers. In addition, Kristianpoller found that this thermoluminescence peak could be optically re-excited with 3 eV and 5.4 eV light which does not occur in the present case. It seems, therefore,

that the thermoluminescence peak does not correspond to the TSC peak and the nature of the carrier responsible for the 273K peak is still unclear.

The remaining TSC peaks in the Linde samples can all be bleached optically following their generation by X-irradiation but are not regenerated with photons following their thermal emptying. The bleaching thresholds range from 1.5 eV to 2.5 eV which are below the energy necessary for electron photoinjection from the sample electrodes.

Turner and Crawford[6] have made some preliminary thermoluminescence measurements on Linde samples and conclude that a thermoluminescence peak that appears at circa 400K is due to the annealing of the V_{OH}^- center. This suggests that the 405K TSC peak observed in the present measurements is due to this defect. The optical bleaching threshold of 2.5 eV also corresponds to the position of the optical absorption band associated with this defect. Although the effective charge of the V_{OH}^- center when occupied by a hole is similar to that of the V^- center and the removal of the hole leaves a center with a two minus effective charge, the remaining defect will not give rise to a thermally stimulated current peak corresponding to that of the V^{2-} center since the remaining charge deficit is associated with the OH^- ion at an oxygen site rather than an additional trapped hole. The small peak at 504K may be due to the V^{2-} defect with the corresponding V^- TSC peak being lost under the larger peaks at 365 and 405K, however, this center could be bleached by 2.1 eV light whereas in the Meller sample the TSC peak believed to be associated with the V^{-2} defect was not bleached. This peak, together with the 210K and 365K peaks may therefore be due to holes trapped at other impurities associated with an aluminum vacancy.

It is clear that the above assignments of TSC peaks to particular
lattice defects are tentative. The impurity content of the sets of samples
from the different initial sources is clearly different and this has a
dominant effect on the TSC spectra and their response to optically induced
charge redistribution. To further clarify these assignments, measurements
are needed on samples in which the impurity content and defect structure
have been modified in a controlled manner. However, it does appear that the
hole traps in bulk Linde Al_2O_3 have similar thermal and optical properties
to those observed in the MOS substrates and felt to be responsible for the back
channel leakage currents. The mechanism by which hole trapping at these lattice
defects caused the back channel leakage is, however, not straight forward since
the defect centers are negatively charged even when occupied by holes. This
implies that the interface region of the Al_2O_3 has lattice defects that are
largely charge compensated prior to any radiation exposure. For example, if
silicon diffuses into the Al_2O_3 lattice substitutionally on an Al^{3+} site
during a processing stage and has an effective 4+ charge, compensation of
three such silicon ions can be achieved by the creation of an Al^{3+} vacancy.
The presence of this defect in the lattice will then permit hole trapping on
adjacent oxygen ions. The trapped holes will reduce the effective negative
charge of the Al^{3+} site and it will no longer compensate the excess positive
charge of the Si^{4+} impurity ion. This excess positive charge corresponds in
magnitude to the number of trapped holes (although it is associated with
different sites in the lattice) and is capable of causing the back channel
leakage currents. Bleaching of the holes from the defect centers either
optically, thermally or by interaction with electrons injected into the lattice,
will restore the charge compensation and hence reduce the leakage currents. It

is possible that the interface region will not be completely ionically compensated at the end of the device fabrication process in which case an excess of Si^{4+} ions in the lattice could create a back channel leakage current prior to any X-irradiation. This might be the case for a device in which a dry oxidation step has been employed. Aluminum vacancies would still be present in the interface region but would be insufficient in quantity to compensate the Si^{4+} introduced into the lattice by diffusion. Since no radiation exposure had occurred, no holes would be trapped at these Al^{3+} vacancy sites. In order to neutralize the excess positive charge it would be necessary to trap electrons in the interface region. This might be achieved by changing the valence state of impurities such as Chromium in the Al_2O_3 but as indicated by the radiation results, electron trapping does not occur with high probability. If such a device was exposed to photons capable of removing holes from V—centers in the Al_2O_3 no change in the back channel leakage current would occur since the hole centers are unoccupied. This behavior is consistent with the observations of Harari and McGreivy[23]. Exposure of such a device to ionizing radiation would populate the hole traps, reduce the compensation of the aliovalent ions provided by the aluminum vacancies and consequently increase the leakage currents. This additional leakage current would be sensitive to low energy photons capable of removing holes from their traps.

Another possible source of interfacial hole trapping that could give rise to back channel leakage currents in a more direct manner than that discussed above, is due to impurities such as Chromium that can change their valence state by either hole or electron capture. If Chromium is present substitutionally on Aluminum sites in the 3+ state it has no effective charge with respect to the normal lattice. When such a site captures a hole and

changes to a 4+ state it has an effective positive charge and may therefore cause back channel leakage behavior. Sites of this type compete with V-center defects for hole trapping and Lee et al.[5] have shown after γ irradiation to 10^5R, 25% of the Cr^{3+} present in Al_2O_3 has changed its valence state. Neutron activation analysis of the samples used in the present measurements indicates a Chromium content of circa $10^{17}cm^{-3}$ which would give rise to about 10^{13} such sites with 2μ of the heterojunction. It is worth noting, however, that thermal bleaching studies by Lee et al. indicated the changed valence state of the Cr^{3+} was stable to about 550K. This is considerably above the temperature at which it has been found that the back channel leakage currents can be reduced by thermal treatment of the SOS samples and may indicate that ions of this type are not responsible for the leakage behavior.

V. CONCLUSIONS

1. Radiation induced hole trapping in Al_2O_3 is responsible for increased back channel leakage behavior.

2. The major hole trap has a thermal depth of 0.8 eV and holes may be removed from this level by photons having energies of 2.5 eV.

3. The positive charge in the Al_2O_3 may be neutralized by electron injection from the Si into the Al_2O_3 as suggested by the reduction of the leakage currents in a device following X-irradiation with all electrodes grounded.

4. Hole traps in Al_2O_3 are mainly associated with aluminum vacancies and even when occupied by holes have effective negative charges. These traps cannot be directly responsible for the observed leakage currents.

5. The aluminum vacancy defects charge compensate excess positive ionic impurities in the Al_2O_3 matrix. When holes are trapped at the Aluminum vacancy defects this charge compensation is reduced and it is the excess ionic charge in the interface zone that is responsible for the back channel leakage.

6. A contribution to the pre-irradiation leakage currents in SOS structures may arise from lack of ionic compensation at the Si/Al_2O_3 heterojunction. This component of the leakage current should be insensitive to "bleaching" by low energy photons since these will not change the valence state of the impurity ions carrying the excess positive charge and the aluminum vacancy hole-traps are unoccupied.

7. The different time/temperature profiles associated with wet and dry oxidation steps would give rise to significantly different diffusion depths for impurities from the silicon into the Al_2O_3. Sample calculations based on the measured diffusion coefficients for oxygen in Al_2O_3 and "typical" oxidation parameters indicate only a 30 $\overset{o}{A}$ penetration for wet oxidation conditions and a 100 $\overset{o}{A}$ penetration under dry oxidation conditions.

8. Alumino-silicate structures seem to be possible at the heterojunction either as a result of chemical reactions occurring during silicon deposition or as a result of solid state diffusion processes. Phases such as Al_2SiO_5 or Mullite $(3Al_2O_3:2SiO_2)$ may exist in conjunction with Al_2O_3 at the heterojunction. Since hole traps are largely dependent on the local lattice co-ordination these other phases might be expected to have traps similar to these found in Al_2O_3.

9. Ions such as Cr^{3+} do compete with the Aluminum vacancy defects for hole capture. These centers are present in commercial Al_2O_3 in concentrations on the order of $10^{16} \to 10^{17} cm^{-3}$. Changes in their valence state as a result of

hole capture will give rise in a direct way to the back channel leakage behavior. The thermal stability of these centers would, however, suggest that they are not responsible for the observed behavior unless electrons released from electron traps in the Al_2O_3 annihilate them at the low temperatures observed in SOS structures.

10. Thermally stimulated current measurements and a tentative identification of the TSC peaks with specific hole and electron traps suggest that the V_{OH}^--centers and some other unidentified hole center in Linde sapphire may be responsible for the back channel leakage behavior. Hydrogen pretreatment of Al_2O_3 would be expected to increase the V_{OH}^- concentration and hence aggravate the back channel leakage problem.

11. Al_2O_3 from different vendors has a different trap structure. Experiments with SOS devices fabricated using the same technology on sapphire from different sources would be important in determining the dependence of radiation hardness on the starting substrate material as distinct from the processing steps of silicon deposition and device fabrication.

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FIGURE CAPTIONS

Fig. 1. Models for hole traps in Al_2O_3

 a) Ideal Crystal b) A V-center defect c) A V_{OH}^--center defect

Fig. 2. Dose and bleaching dependence of leakage currents in a
4007 CMOS/SOS structure.

Fig. 3. Spectral dependence of leakage current reduction in a
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Fig. 4. Time dependence of the leakage current reduction with device
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Fig. 5. Dependence of the leakage current on time of isothermal
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Fig. 6. Thermally Stimulated Current Spectra for Al_2O_3 samples from
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Al_2O_3 from various sources.

Table 2. Optical Bleaching and Trap Refilling Thresholds for Linde
and Meller samples.

VOID

Al^{3+}
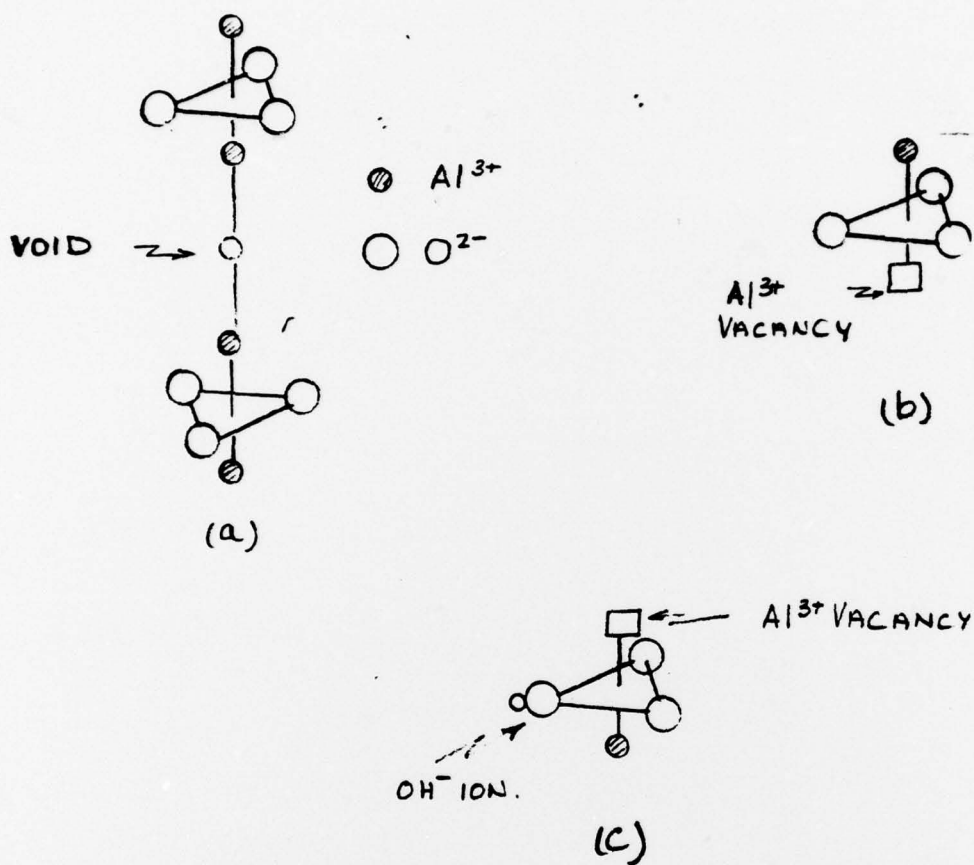
O^{2-}
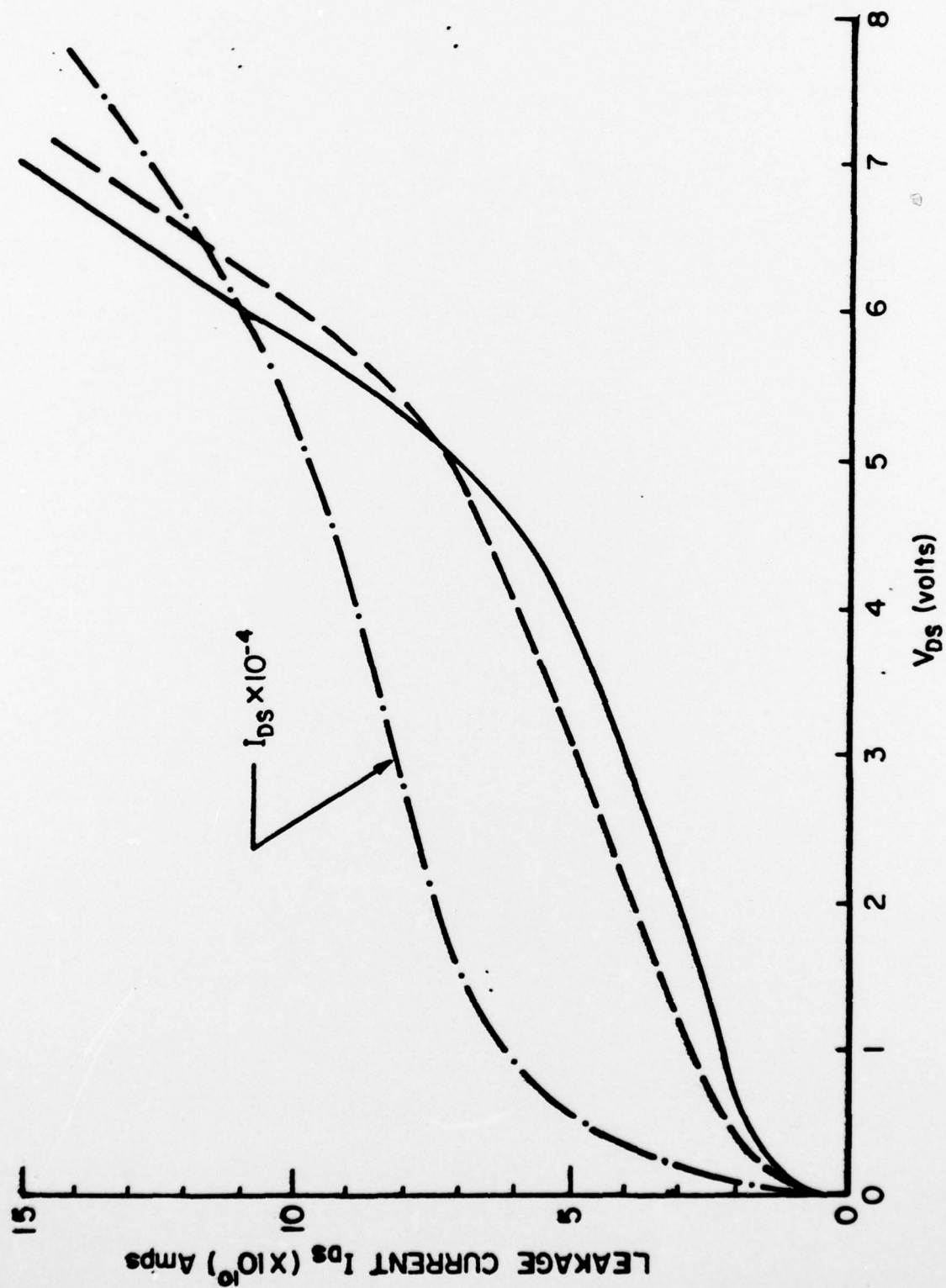
(a)
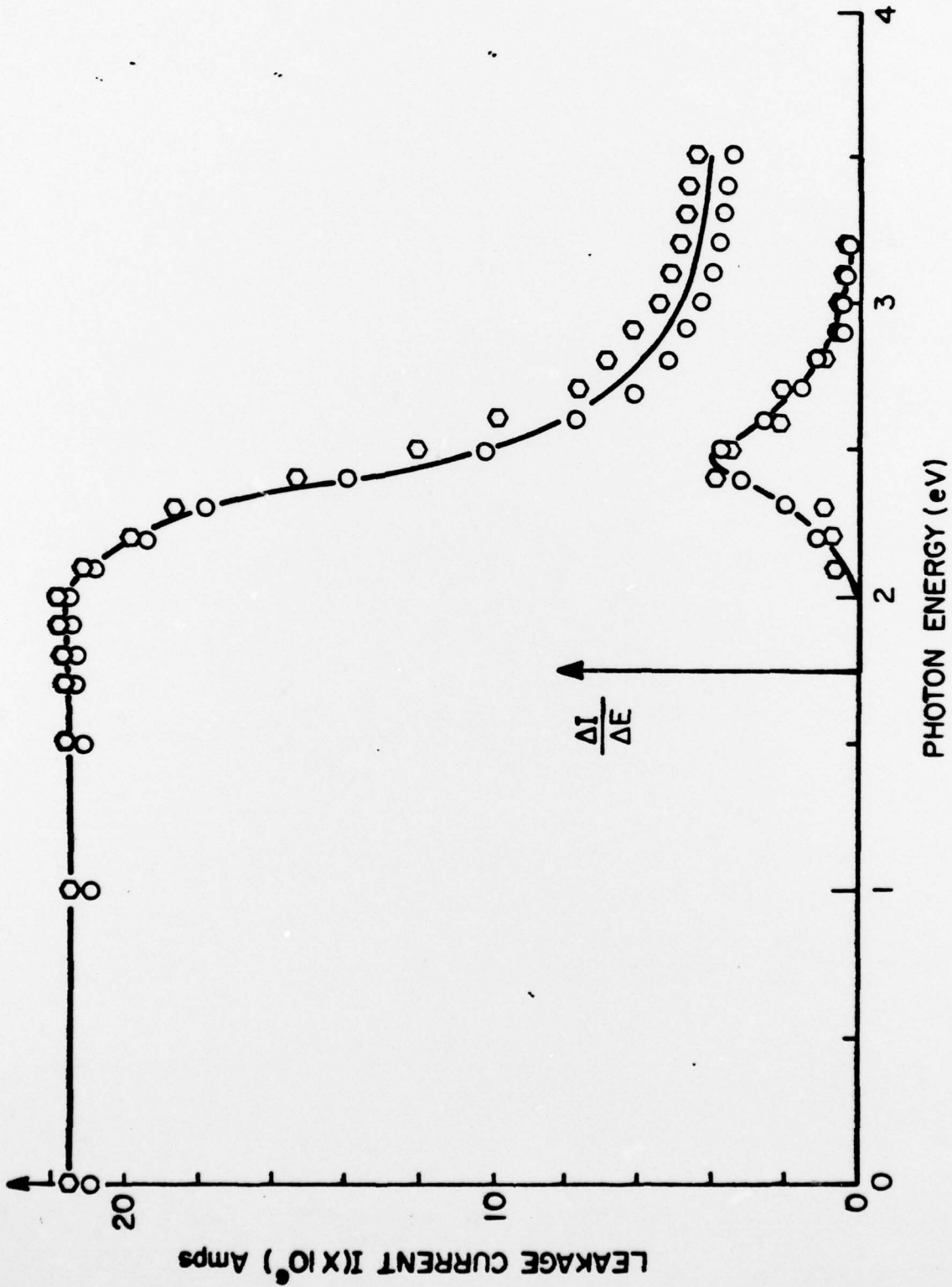
Al^{3+}
VACANCY

(b)

Al^{3+} VACANCY

OH^- ION.

(c)

Figure 1

$I_{DS} \times 10^{-4}$

LEAKAGE CURRENT I_{DS} ($\times 10^{10}$) Amps

V_{DS} (volts)

Figure 2

LEAKAGE CURRENT I(x10⁶) Amps

PHOTON ENERGY (eV)

$\frac{\Delta I}{\Delta E}$

Figure 3

LEAKAGE CURRENT (x10⁶) Amps

ILLUMINATION TIME (mins.) AT 2.5 eV
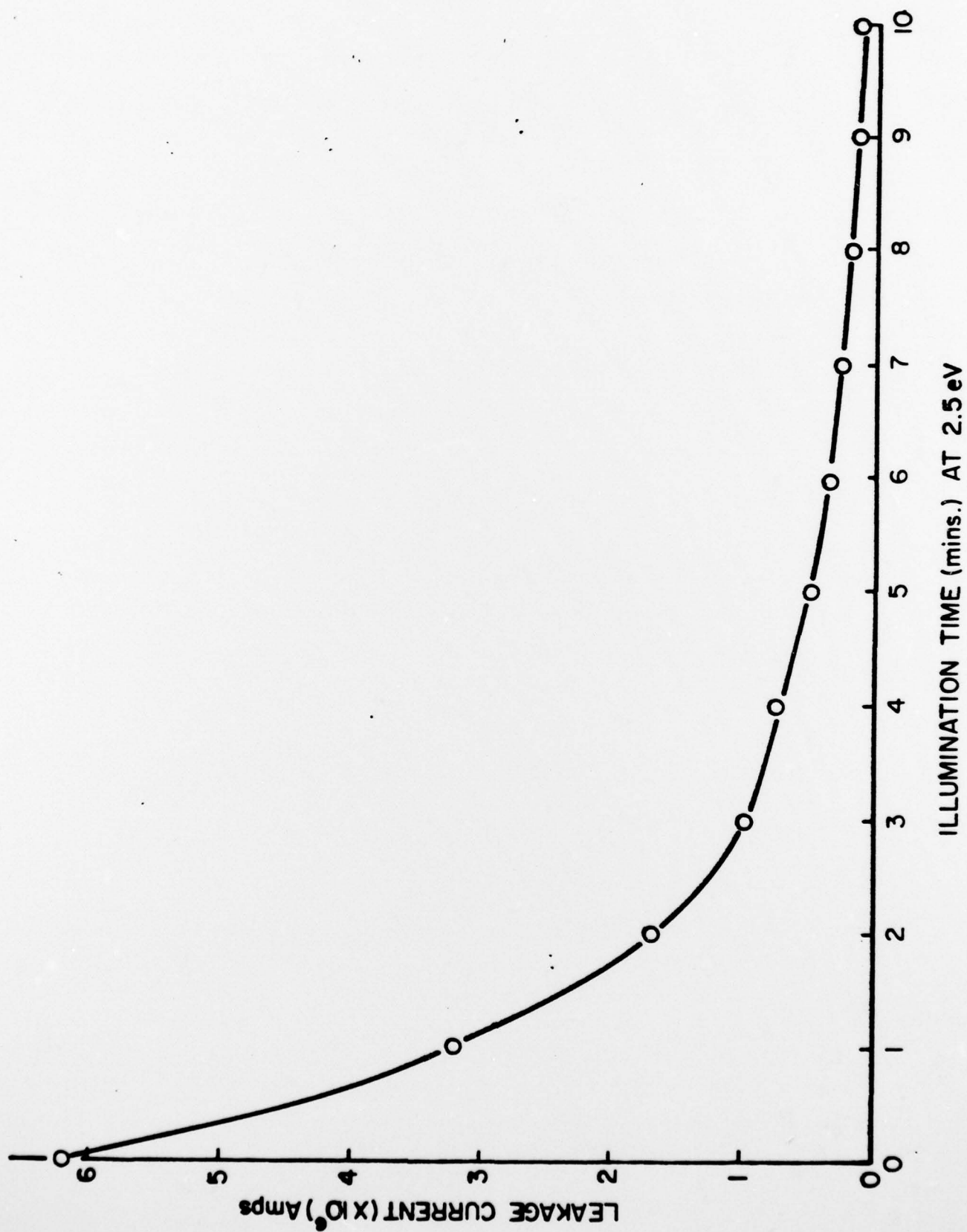
Figure 4

Figure 5

Figure 6

NORMALIZED PEAK HEIGHT (ARB.UNITS)

◇ 372K PEAK
□ 437K PEAK
○ 495K PEAK
△ 560K PEAK

MAXIMUM PHOTON ENERGY (eV)
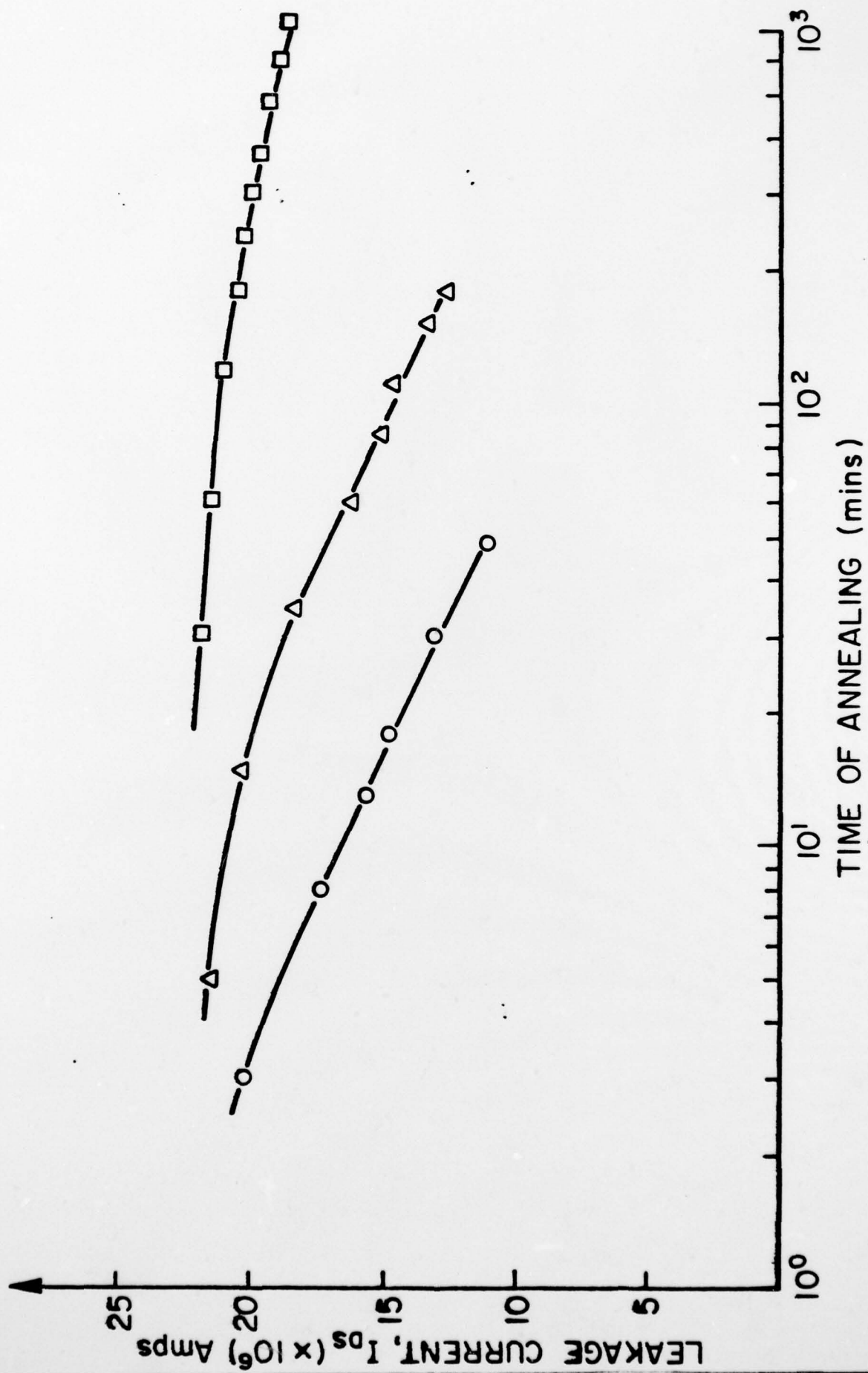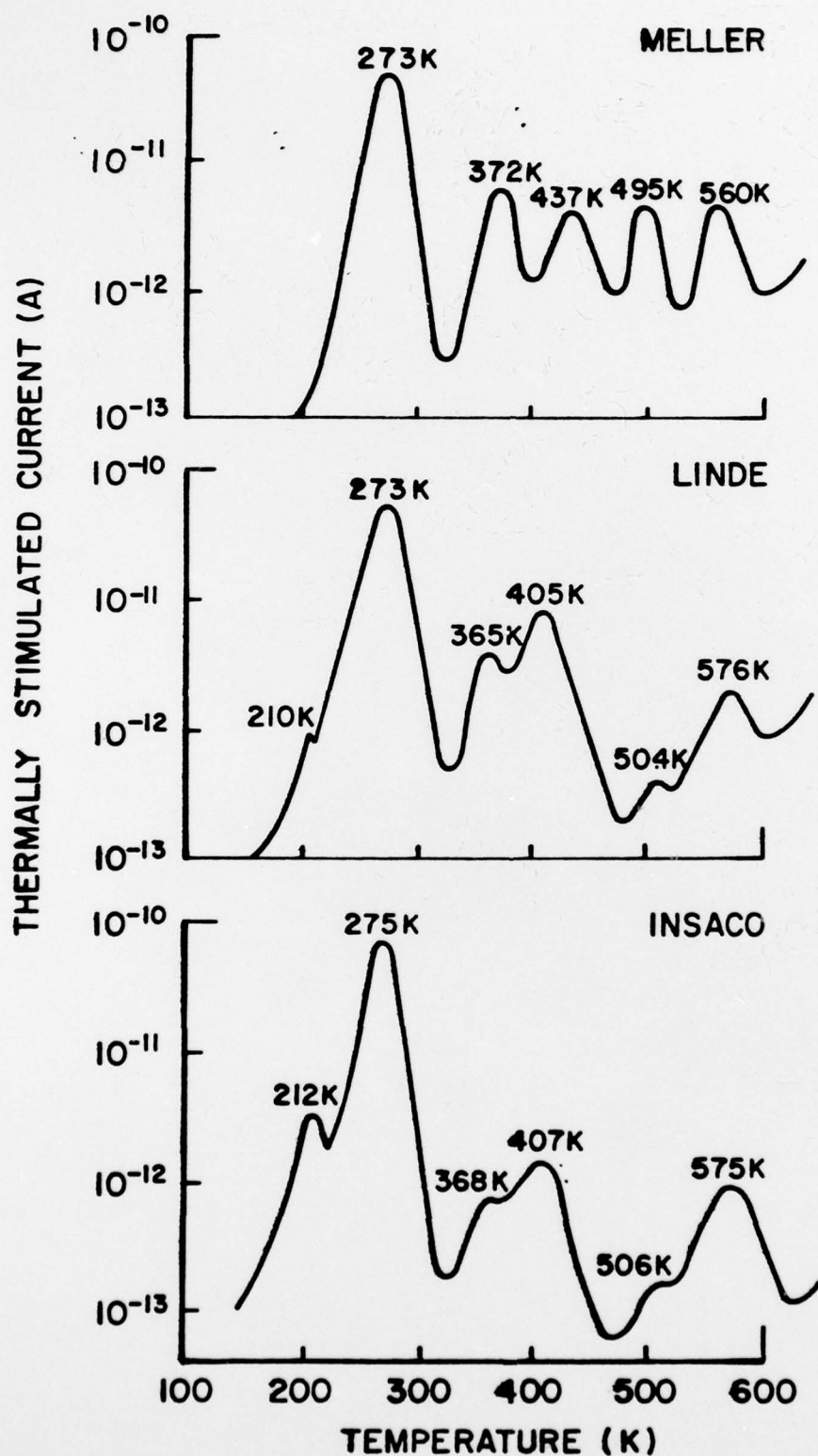
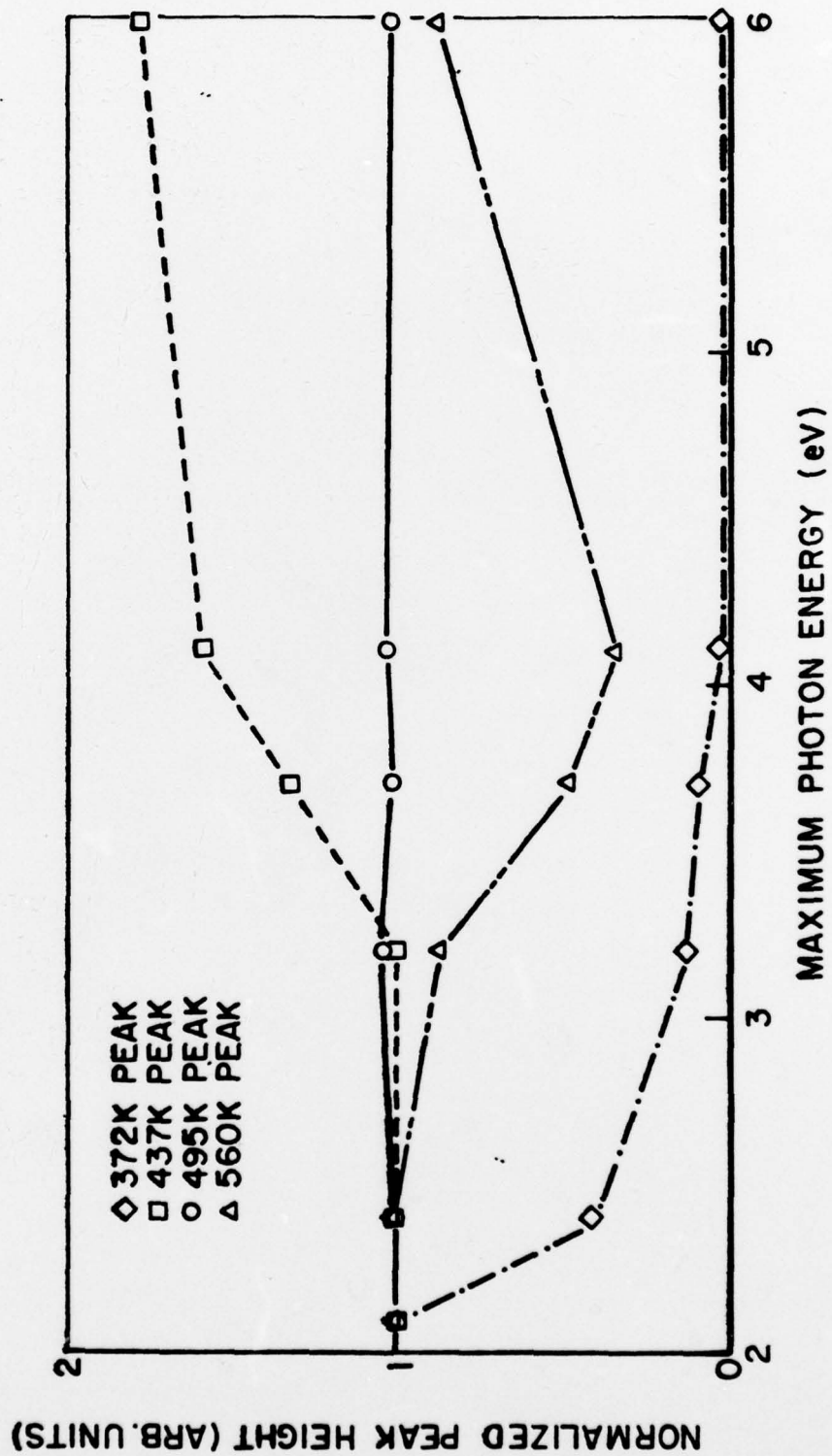Figure 7

TABLE 1

TRAP PARAMETERS FOR THERMALLY STIMULATED CURRENT PEAKS IN Al_2O_3

Material Source	T_{max} (K)	Low Temp Half Width (K)	Energy (eV)	Frequency Factor (sec-1)
INSACO	212	13	0.38 ± 0.05	2×10^7
	275	18	0.48 ± 0.05	1×10^7
	368	20	0.80 ± 0.1	2×10^9
	407	24	0.85 ± 0.1	4×10^8
	506	22	1.37 ± 0.1	1×10^{11}
	575	26	1.50 ± 0.1	1×10^{11}
LINDE	210	13	0.36 ± 0.05	1×10^7
	273	20	0.42 ± 0.05	7×10^6
	365	19	0.83 ± 0.1	4×10^9
	405	23	0.86 ± 0.1	6×10^8
	504	22	1.38 ± 0.1	4×10^{12}
	576	26	1.50 ± 0.1	1×10^{11}
MELLER	273	21	0.42 ± 0.05	7×10^6
	372	18	0.84 ± 0.1	3×10^9
	437	21	1.12 ± 0.1	1×10^{11}
	495	21	1.43 ± 0.1	5×10^{12}
	560	21	1.74 ± 0.1	6×10^{13}

TABLE 2

OPTICAL BLEACHING AND TRAP REFILLING FOR LINDE AND MELLER SAMPLES

Material	T_{max}	Bleaching Energy	Δ	Repopulating Wavelength	Δ
LINDE	210	1.9	-	up to 6 eV	0
	273	up to 6 eV	0	up to 6 eV	0
	365	1.5	-	up to 6 eV	0
	405	2.5	-	up to 6 eV	0
	437 *	---		2.7	+
	504	2.1	-	—	
	576	up to 6 eV	0	2.7	+
MELLER	273	up to 6 eV	0	2.7	+
	372	2.4	-	up to 6 eV	0
	437	3.5	+	2.3	+
	495	up to 6 eV	0	up to 6 eV	0
	560	2.6	-	2.8	+

Δ

+ → increase in peak size

- → decrease in peak size

0 → no change in peak size or no repopulation

* → only appears with optical repopulation